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Photocatalytic degradation of saccharin under UV-LED and blacklight irradiation

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Abstract

BACKGROUND: The photocatalytic treatment of the artificial sweetener saccharin (SAC), an emerging environmental contaminant, was investigated. UVA irradiation was provided by an environmentally friendly light-emitting diode (UV-LED), whose efficiency was compared to a conventional blacklight fluorescent lamp (UV-BL).

RESULTS: The effect of the initial SAC concentration (2.5-10 mg/L), TiO₂ concentration (0-500 mg/L), water matrix (absence/presence of humic acids), and treatment time on process efficiency was evaluated. At the best conditions assayed ([SAC]₀=2.5 mg/L, [TiO₂]=250 mg/L), SAC was degraded within 20 and 90 min under UV-LED and UV-BL irradiation, respectively. Liquid chromatography-high resolution mass spectrometry (LC-HR/MS) revealed that SAC degradation proceeds via hydroxylation of the phenyl ring, cleavage of C-N bond and further oxidation reactions. Finally, UV-LED was found to be up to 16 times more energy efficient than UV-BL.

CONCLUSIONS: In all cases, UV-LED achieved higher photocatalytic efficiency, in terms of organic degradation, and found to be significantly more energy and cost efficient than conventional UV-BL irradiation source, thus rendering LED-photocatalysis a sustainable technology for the treatment of persistent contaminants.

Keywords: Advanced oxidation processes; photocatalysis; wastewater treatment; UV-LED; humic acids; artificial sweeteners; energy consumption

1 INTRODUCTION

2 Artificial sweeteners (ASs) have been recently recognised as emerging micro-contaminants
3 due to their increasing consumption, environmental persistence and widespread detection in
4 the water cycle. ¹ ASs are high production volume chemicals used worldwide to sweeten
5 beverages, personal care products and pharmaceuticals. ^{2,3} Municipal wastewater effluents are
6 the main entrance pathway of ASs in the aquatic environment and among them, saccharin
7 (SAC), acesulfame (ACE) and sucralose (SUC) are widely detected, at trace level
8 concentrations, in groundwater, surface and drinking water. ^{1,4-7} The unawareness of ASs' long-
9 term ecotoxicological effects and their reported formation of toxic by-products during natural
10 attenuation, raise some important environmental concerns ^{5,8} and further call for the
11 development of highly efficient treatment methods.

12
13 TiO₂-mediated photocatalysis, an advanced oxidation process with well-proved efficiency in
14 degrading recalcitrant, non-biodegradable compounds ^{9,10}, has been recently studied for the
15 degradation of SUC, ACE and SAC and the obtained results are encouraging. ^{8,11,12} In principle,
16 photocatalytic oxidation is initiated upon UV illumination of TiO₂; highly reactive species,
17 mainly hydroxyl radicals (HO[•]), are then formed and non-selectively attack organic pollutants,
18 which are subsequently mineralized into CO₂ and harmless inorganic products. ^{13,14} Blacklight
19 (BL) fluorescent UV lamps are commonly used as irradiation source in photocatalytic
20 applications. Nevertheless, these are energy intensive devices and pose environmental hazards
21 due to their content in toxic chemicals (i.e. mercury and lead). ¹⁵ As a result, high operational
22 cost and increased environmental impact hinder the large-scale application of photocatalytic
23 process. ¹⁶ On this basis, UV light-emitting diodes (UV-LEDs) attract considerable attention
24 as eco-friendly alternatives to UV-BL lamps. LEDs' energy efficiency, extended lifetime and
25 less toxic nature (i.e. mercury and lead-free) can lower the cost and improve process

sustainability^{17,18} while their small footprint, directional light output and narrow band emission spectra allow for flexible design and development of compact water treatment units.¹⁹

UV-LEDs were firstly employed by Chen et al. (2005) for the photocatalytic treatment of perchloroethylene²⁰ and since then LED-photocatalysis has been proved feasible for the treatment of a wide range of contaminants. Development of LED photocatalytic reactors has attracted increasing attention recently. UV and visible LEDs of different irradiation wavelengths have been tested, in various configurations (i.e. flexible LED strips, LED arrays, single LEDs, etc.) and reactor set-ups (i.e. LEDs placed above, wrapped around, mounted on, immersed in the reactor, etc.).²¹⁻²⁵ Several studies have also compared the efficiency of LEDs with germicidal and blacklight lamps in photocatalytic applications.²⁵⁻²⁸ However, the comparison has been usually made between irradiation sources of different electrical power or at reactor geometries optimised for U shaped lamps, without considering LEDs' optical characteristics. The directivity of LEDs' affects dramatically the irradiation uniformity²⁴ and when integrated within the reactor in a close distance from catalyst the non-uniform irradiation of the latter results in lower oxidation rates compared to blacklight lamps, as has been previously reported by Levine et al (2011).²⁸ Therefore, a study evaluating a UV-LED relatively to a UV-BL at a set-up providing uniform irradiation, at the same spectral irradiance, electrical power and reactor geometry, in terms of organic removal, energy consumption and under a variety of photocatalytic conditions is still missing from literature.

As a result, the aim of the present study is the investigation of photocatalytic degradation of SAC, the forerunner of ASs with the most diverse uses (i.e. additive in piglet feed²⁹ and brightener in nickel plating³⁰), under UVA irradiation emitted from either a UV-LED or UV-BL lamp. For this purpose, a UV-LED and a UV-BL fluorescent lamp of the same electrical

power and peak emission wavelength were tested in parallel experimental series, under identical photocatalytic conditions (i.e. initial SAC concentration, TiO₂ concentration and water matrix). The influence of key operational parameters, such as the initial SAC concentration, TiO₂ concentration, water matrix, treatment time and irradiation source on photocatalytic performance was assessed. The main transformation products (TPs) under UV-LED and UV-BL irradiation were identified and possible degradation pathways were elucidated. Finally, the energy efficiency of both irradiation sources was evaluated and a comparative study was carried out. To the best of the authors' knowledge, this is the first study employing LEDs for the photocatalytic treatment of ASs.

MATERIALS AND METHODS

Chemicals

All chemicals in this study were of analytical grade and used without further modification. SAC (CAS No: 81-07-2) was purchased from Acros. Leonardite humic acid IHSS standard was used and a stock solution was prepared by dissolving the proper amount of HA in 0.1 M NaOH and further diluting it in deionised water. Aeroxide TiO₂ P25, supplied by Evonik Industries, was used as the photocatalyst because of its higher photocatalytic efficiency among other commercial catalysts, as was found also in our previous study.¹²

Photocatalytic experiments

Experiments were conducted in a batch-operated slurry photoreactor, applying a working volume of 150 mL. For LED driven photocatalysis, a UVA emitter ($\lambda_{\text{max}}=365$ nm; LZ4-00U600, LED Engin) was employed and mounted onto a heat sink to prevent radiant flux decrease due to temperature rise. The LED assembly (Schematic 1) was placed directly above the reactor and a quartz protective plate was placed between them. The second irradiation

source was a UV-BL fluorescent lamp ($\lambda_{\text{max}}=365$ nm; PLS G23, Casell Lighting), housed in a quartz tube and, for the sake of comparison, positioned on top of the photoreactor, at the same height as UV-LED. Both set-ups were covered with an aluminium shield to prevent any light diffusion out of the reactors and to minimise penetration of ambient light. The quartz glasses were used to protect the lamps from water spills. UV-LED and UV-BL irradiation sources were driven by electrical power of 11W and were connected in series to a DC power supply.

Schematic 1

In a typical run, SAC solution (2.5-10 mg/L) was loaded in the photoreactor and the desired amount of catalyst was added. The slurry solution in the reactor was continuously stirred at 500 rpm with a magnetic stirrer to promote uniform dispersion of the photocatalyst powder and dissolved oxygen. At the beginning of each experiment, the solution was stirred in the dark for 30 min to ensure adsorption-desorption equilibrium of SAC on TiO_2 surface. The UV source was then switched on and at regular time intervals samples were withdrawn and filtered through 0.45 μm syringe filters to separate catalyst particles and further analysed in terms of their SAC concentration. All experiments were conducted at room temperature and at the natural pH of SAC solutions (~ 4.6). After 45 min of treatment, solution's temperature was found to increase by 3° C (from 21 °C to 24 °C) under both irradiation sources.

Analytical techniques

SAC concentration in filtrate samples was measured by a high performance liquid chromatography (HPLC) system (S200 Pump, S225 Autosampler, Perkin Elmer) coupled with a diode array detector (S200 EP, Perkin Elmer) with a limit of detection (LOD) and limit of quantification (LOQ) of 0.005 and 0.1 mg/L, respectively. Separation was performed on a

reverse phase C18 analytical column (Luna® Phenomenex 5u, 250 x 4.6 mm). HPLC method for SAC was obtained from Trandafil et al. (2009)³¹ and was appropriately modified. The mobile phase consisted of 85 vol. % 0.02 M KH₂PO₄ and 15 vol. % CH₃CN fed at a flow rate of 1 mL/min. The elution was isocratic and the injection volume was 40 µL. The detection wavelength was at $\lambda=216$ nm.

The photon flux emission of the irradiation sources was determined by potassium ferrioxalate actinometry, as described by Murov³², and found to be 3.32×10^{-6} and 3.15×10^{-7} Einstein/s for UV-LED and UV-BL lamp, respectively. The spectral distribution of UV-LED and UV-BL was measured by a Labsphere E1000 spectral irradiance receiver with a concentrator area of 1 cm² and are presented in Figure 1.

Figure 1

A Bruker micrOTOF Focus II interfaced to a Dionex (Thermo Scientific) Ultimate 3000 UHPLC system was used for the identification of SAC TPs. The chromatographic separation was performed using a Thermo Scientific AcclaimTM RSLC 120 C18 column thermostated at 30° C. The mobile phase consisted of LC-MS grade water-0.01% formic acid (A) and LC-MS grade acetonitrile (B) with a flow rate of 0.25 ml/min. The following elution was adopted: A/B: 99/1 (0 min), A/B: 1/99 (15 min), A/B: 99/1 (17 min), A/B: 99/1 (18 min). The micrOTOF Focus II was operated in negative ionization mode. Dry gas at 8 L/min, nebulizer press at 2.4 bar, dry heater at 200° C, hexapole RF at 100 Vpp and capillary were adjusted at 4200 V.

Energy consumption

The energy consumption of artificial lighting constitutes a major fraction of the operating costs in UV photocatalysis. Bolton et al. (2001) introduced the electric energy per order, E_{EO} , defined as the energy required for 90% degradation of a pollutant per cubic meter of contaminated water. ³³ E_{EO} (kWh/m³/order), for a batch-operated reactor, is calculated from the following equation:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_i/C_f)} \quad (1)$$

where P is the electrical power of the irradiation source (kW), t is the irradiation time (min), V is the volume of the treated effluent (L), and C_i and C_f are the initial and the final pollutant concentrations (mg/L), respectively.

RESULTS AND DISCUSSION

Effect of initial SAC concentration

Initial SAC concentration in the range of 2.5-10 mg/L was applied to assess its effect on photocatalytic performance, in the presence of 125 mg/L TiO₂. In both cases, the pseudo-first-order reaction model was found to describe well the photocatalytic removal of SAC (Table 1). As seen in Figure 2, increase in the initial SAC loading resulted in decreased removal efficiency. Specifically, increase of SAC concentration from 2.5 to 10 mg/L led to removal decrease from 99.9 to 86.1% (with $k=0.198-0.043$ min⁻¹) during UV-LED photocatalysis (Figure 2a) and 71.2 to 35.1% (with $k=0.030-0.010$ min⁻¹) under UV-BL irradiation (Figure 2b). Increase in the initial organic substrate concentration, at a fixed catalyst concentration, lowers the ratio of oxidant species to substrate and further results in decreased degradation yields ³⁴, thus explaining the findings presented above. According to the results, UV-LED could completely degrade up to 5 mg/L of SAC within 30 min of photocatalytic treatment

(Figure 2a). On the other hand, SAC, even at the lowest (2.5 mg/L) concentration, could not be degraded after 45 min of treatment under UV-BL irradiation (Figure 2b).

Table 1

Figure 2

Effect of catalyst concentration

Control experiments (i.e. photolysis and exposure under darkness in the presence of catalyst) were performed to assess the effect of catalyst on process efficiency and its adsorption capacity. As presented in Figure 3, photocatalysis was shown to be the main removal mechanism, since SAC concentration remained almost unchanged after 45 min of photolysis or treatment in the dark.

The effect of catalyst concentration on process efficiency was then investigated by applying various catalyst concentrations (i.e. 125, 250 and 500 mg/L), at 5 mg/L initial SAC concentration. Figure 3a shows that 99.9% degradation of SAC took place within 30 min under UV-LED irradiation, in the presence of all the tested catalyst concentrations and it becomes evident that increase in catalyst concentration beyond 125 mg/L did not further improve the process efficiency. Similarly, as depicted in Figure 3b, catalyst concentration did not affect notably SAC removal under UV-BL irradiation, either. In principle, increase of TiO₂ concentration enhances organic substrate's oxidation by offering more photoactive surface area for adsorption and generation of a greater amount of oxidizing species. However, at higher TiO₂ concentrations removal efficiency becomes independent of catalyst mass, as it was observed in the present study, due to agglomeration of TiO₂ particles and subsequent reduction

in available surface area, as well as, due to increased opacity and light scattering that further reduce the light passage through the solution.¹³

Unlike catalyst concentration, irradiation source had a profound effect on process efficiency. SAC removal was only about 60% after 45 min of treatment under UV-BL irradiation, making it clear that UV-LED was more efficient (i.e. total SAC degradation achieved after 30 min of treatment) in terms of organic removal.

Figure 3

Effect of water matrix

5 and 8 mg/L of humic acids (HA) were added to SAC/TiO₂ system to examine the effect of water matrix on SAC removal and the results are presented in Figure 4. The addition of HA was found to be inhibitory for SAC photocatalytic oxidation, under both types of irradiation, resulting in removal rates up to 3.6 times lower than in the respective SAC/TiO₂ systems. In particular, addition of 8 mg/L HA reduced by 73% the removal rate of SAC, regardless of the light source. Specifically, SAC removal percentages decreased from 99.9% to 27% and 55.1% to 15% under UV-LED and UV-BL irradiation, respectively. The observed removal efficiency may be attributed to a partial expenditure of oxidizing radicals for the degradation of HA by UV/TiO₂^{35,36} that lowers the ratio of oxidant species to SAC molecules and further limits SAC oxidation.

Figure 4

TPs and reaction pathways

For the identification of TPs, additional experiments were conducted at an increased SAC concentration (15 mg/L) in the presence of 250 mg/L TiO₂ for both systems. Accurate mass measurements in negative ionization mode (Table 2) revealed the formation of seven and five TPs during SAC degradation under UV-LED and UV-BL irradiation, respectively. Based on the mass spectra data (m/z [M-H]⁻ ions) and the elemental composition of the deprotonated ions obtained by the mass instrument software as well as the kinetic profiles of the TPs, possible structures and degradation pathways are proposed and shown in Figure 5. According to the results, the photocatalytic transformation of SAC under both irradiation sources, starts by the hydroxylation of the molecule giving rise to the formation of three isomers (TP4, TP5, TP6). The hydroxylation mechanism proposed in the present study is consistent with previous work that reported relatively high reactivity of hydroxyl radicals towards the studied sweetener and proposed that the oxidation mechanism involves the addition of hydroxyl radicals in the aromatic ring, resulting in hydroxylated products ³⁷. Hydroxylation of phenyl ring as well as N atom can be considered. Sequential hydroxylation of the above-mentioned TPs results to di- and tri-hydroxy derivatives (TP7 and TP1). The sequential steps of hydroxylation are also confirmed by the evolution profiles of TPs (Figure 6) revealing that TP7 and TP1 peak concentrations are recorded in longer irradiation times than that of monohydroxylated TPs. Based on the fact that mono-hydroxylated TPs attained their maximum concentration within the first stages of the process, they can be characterized as primary TPs. TP7 and TP1, di-hydroxylated and tri-hydroxylated products, are recorded in longer irradiation times simultaneously with the slower degradation of mono-hydroxylated derivatives, proving the sequential steps of hydroxylation. Their rapid disappearance can be associated with the formation of ring opening products and the favored cleavage of the molecule after successful hydroxylation. TP5 is the most abundant mono-hydroxylated product identified during the

photocatalytic degradation of saccharin and shows a slower degradation rate during the process and a prolonged irradiation time for its complete removal. Cleavage of the C-N bond of sulfonamide group and further oxidation leads also to the formation of TP2 and TP3, bearing amine and/or carboxylic acid functional groups. As depicted in Figure 6, under UV-LED irradiation all the TPs are completely removed between 30-120 min. On the other hand, some TPs remain at trace levels after 300 min of treatment using UV-BL as irradiation source. Short-chain carboxylic acids, such as oxalic, formic, and maleic acid is expected as end-products from the oxidative transformation of SAC primary TPs using advanced oxidation processes as reported elsewhere.³⁸

Table 2

Figure 5

Figure 6

Effect of the irradiation source

It becomes obvious from the results presented so far that the irradiation sources, although driven by the same electrical power and having the same $\lambda_{\text{max}}=365$ nm, resulted in different SAC degradation yields, with UV-LED leading constantly to higher oxidation rates than UV-BL.

Catalysts' activity depends strongly on photon energy (i.e. wavelength) and TiO₂ (P25) is sufficiently photo-activated at $\lambda < 380$ nm.¹³ Figure 1 presents the spectral irradiance distribution of the two light sources; as can be seen, UV-LED has a narrow band emission

centred at about 370 nm so the catalyst can absorb all the incident radiation. However, the broadband spectrum of the UV-BL lamp consists of a higher fraction of photons with $\lambda > 380$ nm that are beyond the action spectrum of catalyst, thus resulting in decreased oxidation rates when compared to UV-LED.

The photon flux is another critical, and possibly the most important, parameter to be considered. Increased photon flux can lead to the formation of more hydroxyl radicals and therefore higher oxidation rates of organic substances.³⁹ As was revealed by potassium ferrioxalate actinometry, the incident photon flux on reactant solution under UV-LED irradiation (i.e. 3.32×10^{-6} Einstein/s) was an order of magnitude higher than that of the UV-BL lamp (i.e. 3.15×10^{-7} Einstein/s), explaining the higher photocatalytic efficiency under UV-LED irradiation. This tenfold gap is due to the different directionality of the light sources. UV-BL lamp emits light in all directions, and even though aluminium foil is used to reflect the irradiation back into the photoreactor, a fraction of the emitted photons is lost. On the other hand, UV-LED produces a directional beam of light so there is no leak of UV light outside the reactor.

Under a closer look, although the light intensity provided by the UV-LED is 10 times higher, k values, during LED-photocatalysis, were 4-9 times higher than those of UV-BL, implying a lower apparent photonic efficiency (i.e. ratio of reaction's rate to the rate of incident photons) than UV-BL. The reaction rate increases linearly with light intensity up to a point and then it increases with the square root of the light intensity^{39,40} due to the higher recombination of the photogenerated electron-hole pairs.⁴¹ That means that increase in light intensity enhances to a lesser extent the process efficiency, thus lowering the photonic efficiency. This tendency has been also reported by Chen et al. (2007) and Coutts et al. (2011)^{40,42} and highlights the need for the right balance between removal efficiency and energy consumption when it comes to the determination of light intensity.

Energy consumption

The energy consumption, E_{EO} , of the two irradiation sources was estimated by Equation (1) and the results are shown in Figure 7. It is observed that UV-LED requires significantly lower E_{EO} values, compared to UV-BL, suggesting its higher sustainability. Specifically, the maximum $E_{EO,BL}/E_{EO,LED}$ ratio (with values up to 16) was found at initial SAC concentration ≤ 5 mg/L. For instance, during the photocatalytic treatment of 5 mg/L SAC in the presence of 125 mg/L TiO_2 , the E_{EO} was estimated at $8.2 \text{ kWh}\cdot\text{m}^{-3}\cdot\text{order}^{-1}$ and $134.4 \text{ kWh}\cdot\text{m}^{-3}\cdot\text{order}^{-1}$ under UV-LED and UV-BL, respectively. In all cases, UV-LED was found to be more energy-efficient than UV-BL photocatalytic treatment, since the first requires less treatment time to achieve SAC removal than the latter.

A cost estimation of the two photocatalytic processes, based on their energy consumption, was attempted. The average electricity price, which is $0.10 \text{ £}\cdot\text{kWh}^{-1}$ ⁴³, purchased by non-domestic consumers in the United Kingdom was used. Under the best conditions assayed, UV-LED treatment costs $0.72 \text{ £}\cdot\text{m}^{-3}\cdot\text{order}^{-1}$. The corresponding cost for SAC removal, under UV-BL irradiation, is $3.3 \text{ £}\cdot\text{m}^{-3}\cdot\text{order}^{-1}$, rendering UV-LED more cost-efficient than UV-BL photocatalysis.

Figure 7

CONCLUSIONS

The photocatalytic treatment of saccharin (SAC), an emerging persistent contaminant, was investigated. Two different UVA irradiation sources, an eco-friendly light-emitting diode (UV-LED) and a conventional blacklight fluorescent lamp (UV-BL), were employed and their

1 photocatalytic performance was compared. The effect of operating parameters, namely initial
2 SAC concentration, TiO₂ concentration, and water matrix on process efficiency was assessed.
3 In addition, intermediate transformation products (TPs) were identified for both irradiation
4 sources and potential degradation pathways were proposed. The conclusions drawn are
5 summarised below.

- 6 - SAC conversion increases with the initial SAC concentration decrease; however, TiO₂
7 concentration does not largely affect the process efficiency.
- 8 - The presence of humic acids (HA) in the reactant solution decreases considerably SAC
9 degradation, under both irradiation sources, indicating the significance of the effect of
10 water matrix on process efficiency.
- 11 - Seven and five TPs were identified for the UV-LED/TiO₂ and UV-BL/TiO₂ system,
12 respectively. The degradation of SAC occurs via (i) hydroxylation of the phenyl ring,
13 (ii) cleavage of the C-N bond and (iii) oxidation reactions.
- 14 - The irradiation source has a critical effect on process efficiency. In all cases, UV-LED
15 yielded higher removal rates than conventional UV-BL irradiation. The superior
16 performance of LED driven photocatalysis is attributed to the higher photon flux
17 reaching the reactant solution due to UV-LED's directionality. Therefore, LED was
18 found to be significantly more energy and cost-efficient than BL photocatalysis.

19 All in all, UV-LED/TiO₂ photocatalytic oxidation is proved to be promising for water treatment.
20 Nevertheless, future efforts should focus on assessing the energy requirements and operating
21 costs of LED-based photocatalysis at real-scale and how this technology can be incorporated
22 into existing water treatment plants. Also, the ecotoxicity of the final effluent should be
23 quantified and comprehensively investigated before any further process scaling-up.

24 25 **Acknowledgements**

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List and captions of Tables

Table 1. Removal percentage (R), reaction rate constant (k), and coefficient of linear regression of data fitting (r^2) for SAC photocatalytic degradation, under UV-LED and UV-BL irradiation.

Table 2. High resolution mass spectra data for SAC and identified TPs derived from mass spectrometric analysis.

Table 1

Operating parameter	Irradiation source	mg/L	R, %	First-order reaction model	
				k, min^{-1}	r^2
Initial SAC concentration ^a	UV-LED	2.5	99.9	0.198	0.996
		5	99.9	0.159	0.995
		7.5	98.4	0.069	0.989
		10	86.1	0.043	0.974
	UV-BL	2.5	71.2	0.030	0.988
		5	55.1	0.018	0.993
		7.5	42.7	0.014	0.981
		10	35.1	0.010	0.960
TiO ₂ concentration ^b	UV-LED	125	99.9	0.159	0.995
		250	99.9	0.170	0.991
		500	99.9	0.163	0.997
	UV-BL	125	55.1	0.018	0.993
		250	61.0	0.022	0.990
		500	58.6	0.018	0.964
Best operating conditions ^c	UV-LED		99.9	0.303	0.998
	UV-BL		85.5	0.044	0.991

^a $[\text{TiO}_2]=125 \text{ mg/L}$; irradiation time=45 min

^b $[\text{SAC}]_0=5 \text{ mg/L}$; irradiation time=45 min

^c $[\text{SAC}]_0=2.5 \text{ mg/L}$; $[\text{TiO}_2]=250 \text{ mg/L}$; irradiation time=45 min

Table 2

LED-driven photocatalytic removal of SAC						
t_R (min)	Code name	Elemental Composition of deprotonated molecule	Theoretical m/z [m-H]⁻	Experimental m/z [m-H]⁻	Δ (ppm)	RDBE
1.6	TP1	C ₇ H ₄ NO ₆ S ⁻	229.9765	229.9756	3.7	6.5
2.3	TP2	C ₇ H ₆ NO ₆ S ⁻	231.9921	231.9917	1.8	5.5
3.3	TP3	C ₆ H ₆ NO ₄ S ⁻	188.0023	188.0025	-0.9	4.5
3.7	TP4	C ₇ H ₄ NO ₄ S ⁻	197.9867	197.9867	0	6.5
4.0	TP5	C ₇ H ₄ NO ₄ S ⁻	197.9867	197.9870	-1.9	6.5
4.1	TP6	C ₇ H ₄ NO ₄ S ⁻	197.9867	197.9867	0	6.5
4.3	TP7	C ₇ H ₄ NO ₅ S ⁻	213.9816	213.9815	0.3	6.5
4.7	SAC	C ₇ H ₄ NO ₃ S ⁻	181.9917	181.9920	-1.4	6.5
Photocatalytic removal of SAC under UV-BL						
t_R (min)	Code name	Elemental Composition of deprotonated molecule	Theoretical m/z [m-H]⁻	Experimental m/z [m-H]⁻	Δ (ppm)	RDBE
2.3	TP2	C ₇ H ₆ NO ₆ S ⁻	231.9921	231.9925	-1.8	5.5
3.7	TP4	C ₇ H ₄ NO ₄ S ⁻	197.9867	197.9871	-2.3	6.5
4.0	TP5	C ₇ H ₄ NO ₄ S ⁻	197.9867	197.9858	4.1	6.5
4.1	TP6	C ₇ H ₄ NO ₄ S ⁻	197.9867	197.9858	4.1	6.5
4.3	TP7	C ₇ H ₄ NO ₅ S ⁻	213.9816	213.9810	2.6	6.5
4.7	SAC	C ₇ H ₄ NO ₃ S ⁻	181.9917	181.9915	1.1	6.5

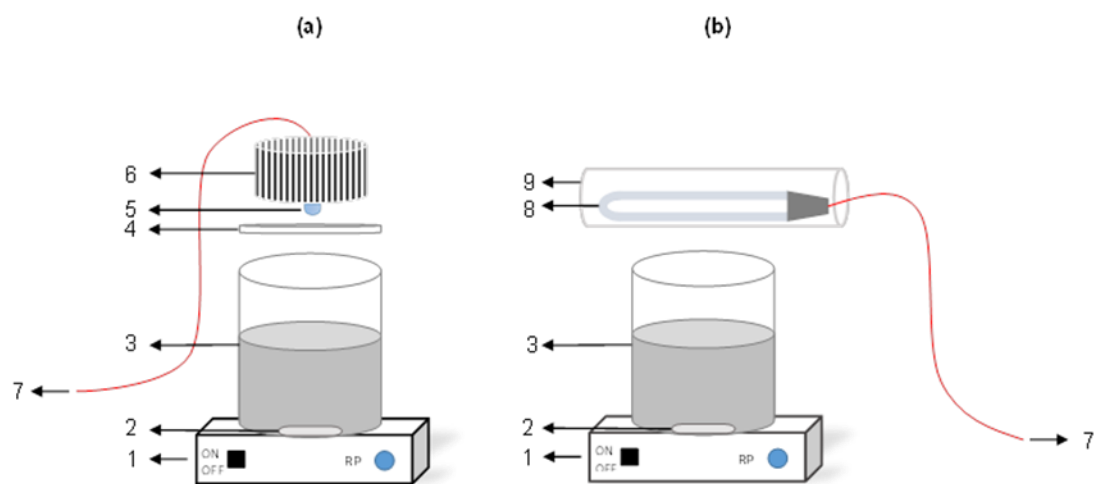
1 List and captions of Schematics

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3 **Schematic 1.** Schematic diagram of (a) UV-LED and (b) UV-BL photocatalytic reactors (1:
4 magnetic stirrer, 2: stirring bar, 3: glass reactor, 4: quartz plate, 5: LED emitter, 6: heat sink, 7:
5 cable connection to DC power supply, 8: BL lamp and 9: quartz sleeve).

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4 Schematic 1.

List and captions of Figures

Figure 1. Relative spectral irradiance of UV-LED and UV-BL.

Figure 2. Effect of initial SAC concentration on its photocatalytic removal under (a) UV-LED and (b) UV-BL irradiation. Experimental conditions: $[\text{TiO}_2]=125 \text{ mg/L}$.

Figure 3. Effect of catalyst concentration on SAC photocatalytic removal and control experiments under (a) UV-LED and (b) UV-BL irradiation. Experimental conditions: $[\text{SAC}]_0=5 \text{ mg/L}$.

Figure 4. Photocatalytic removal of SAC in the presence of different concentrations of HA under UV-LED and UV-BL irradiation. Experimental conditions: $[\text{SAC}]_0=5 \text{ mg/L}$; $[\text{TiO}_2]=125 \text{ mg/L}$; irradiation time=45 min.

Figure 5. Photocatalytic degradation pathways of SAC under UV-LED and UV-BL irradiation.

Figure 6. Kinetic profiles of SAC TPs under (a) UV-LED and (b) UV-BL irradiation. Experimental conditions: $[\text{SAC}]_0=15 \text{ mg/L}$; $[\text{TiO}_2]=250 \text{ mg/L}$.

Figure 7. Electrical energy per order (E_{EO}) under UV-LED and UV-BL irradiation for different initial SAC concentrations. Experimental conditions: $[\text{TiO}_2]=125 \text{ mg/L}$; irradiation time=45 min.

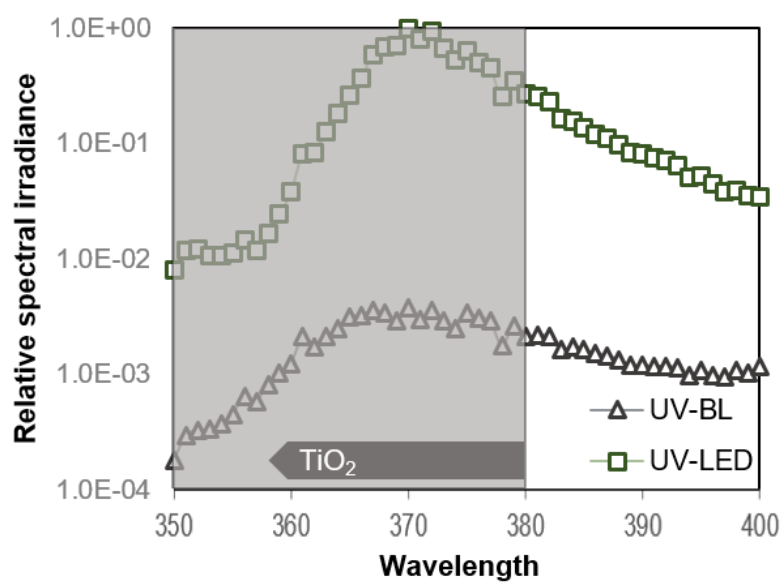
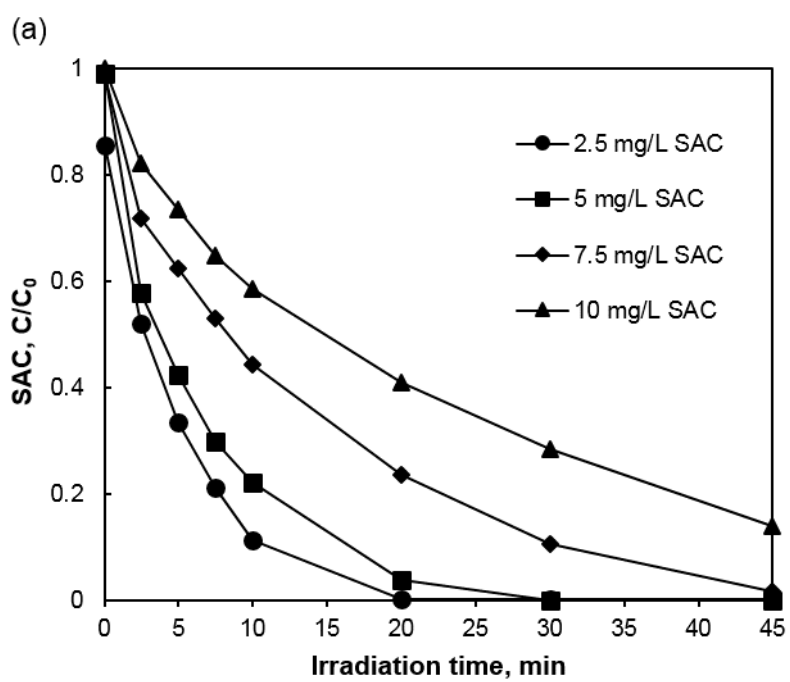


Figure 1



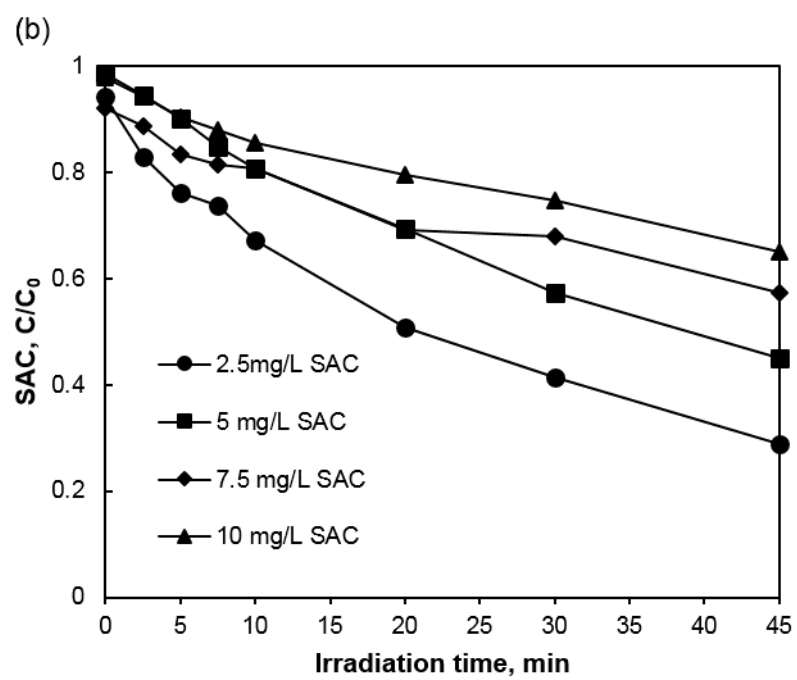


Figure 2

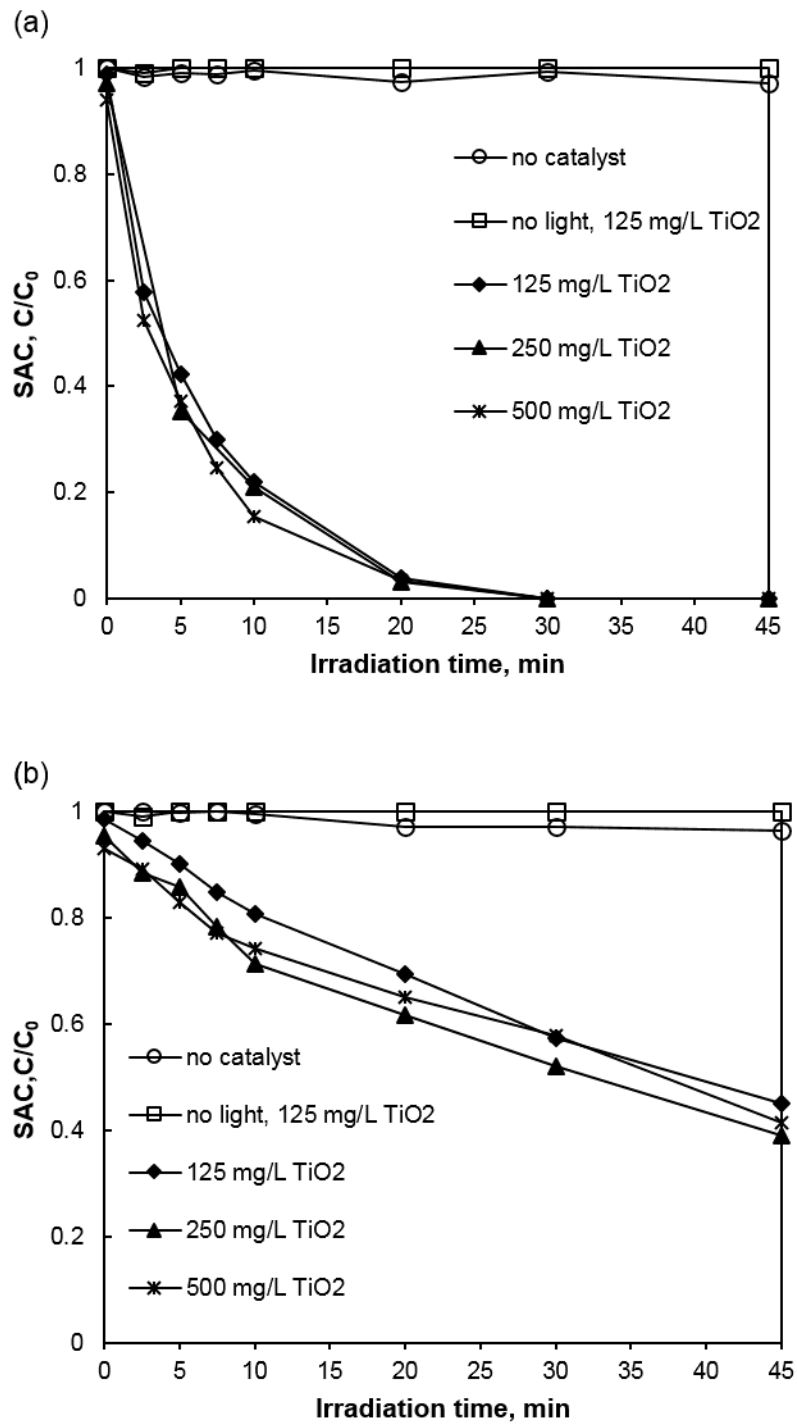


Figure 3

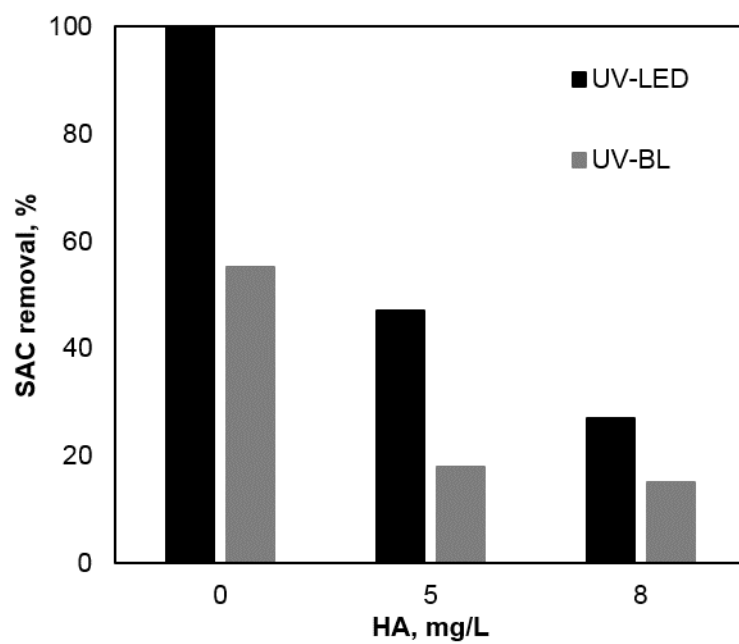


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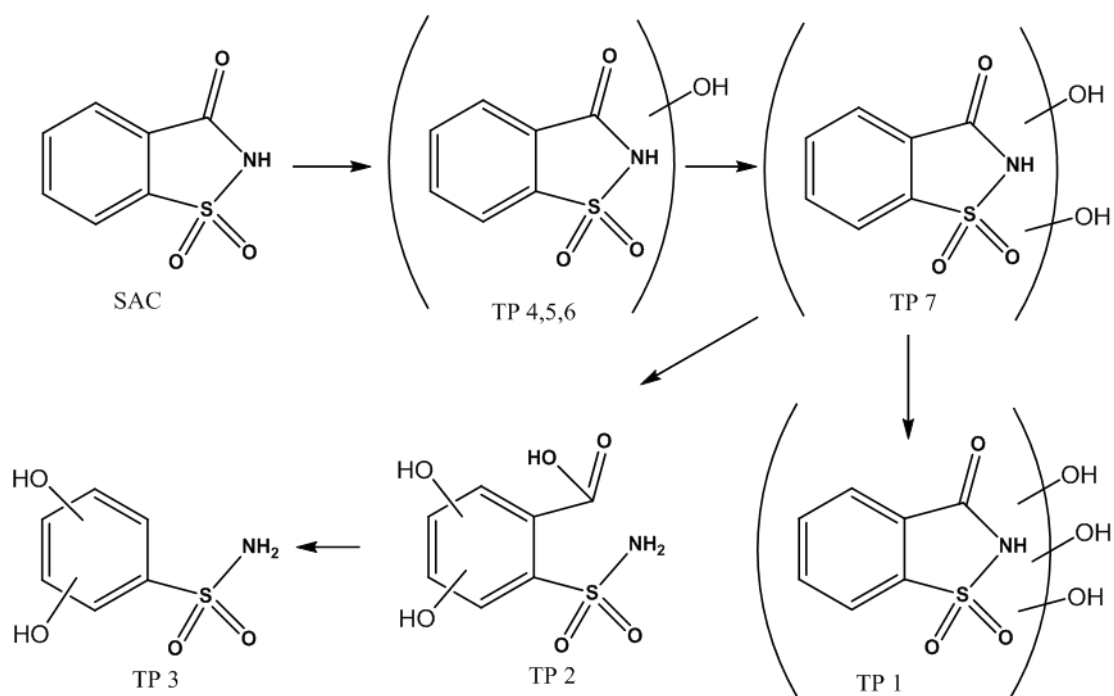


Figure 5

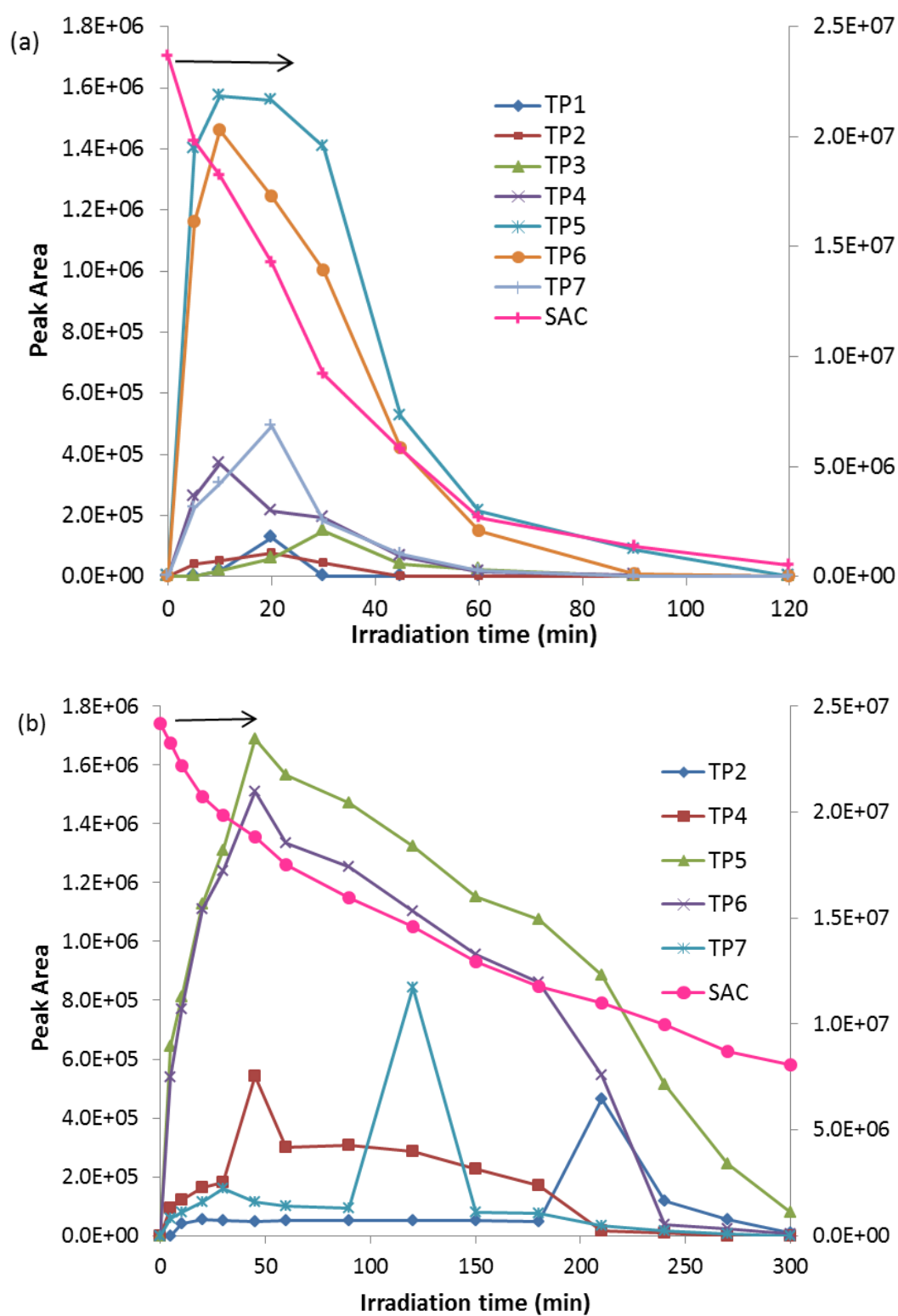


Figure 6

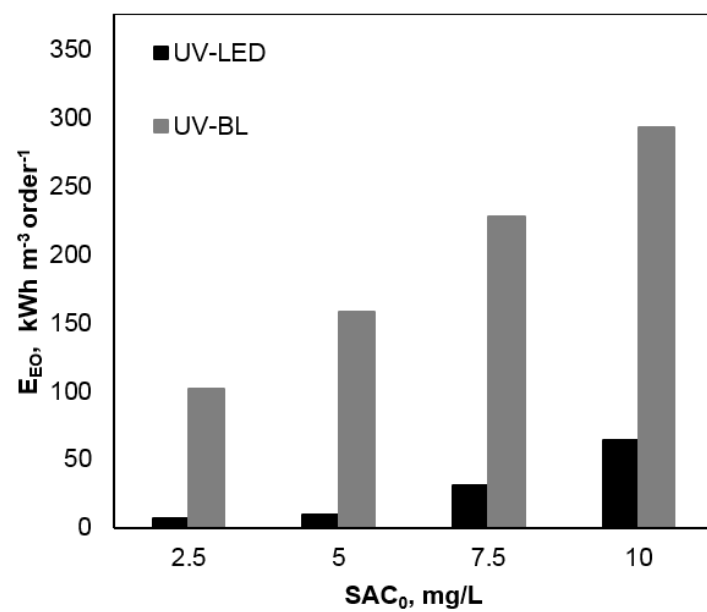


Figure 7